NEW KINETIC APPROACH FOR EVALUATION OF THERMAL HAZARD INDICATORS BASED ON DSC AND LARGE SCALE TESTS

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The estimation of the hazard probability of "reactive or self-reactive chemicals" is a very important issue especially for the safety analysis of many technological processes or packaged materials during transport conditions. The dangerous runaway scenario is quantitatively characterized by the thermal hazard indicators such as the Time to Maximum Rate under adiabatic conditions (TMR_{ad}) and the Self Accelerating Decomposition Temperature (SADT) [1].

Due to the fact that significant amount of heat is evolved during the decomposition of self-reactive chemicals their thermal properties are frequently investigated in laboratory at mg- or g-scales under non-isothermal or isothermal conditions using Differential Scanning Calorimetry (DSC) or, more sensitive, Heat Flow Calorimetry (HFC) techniques.

The elaboration of the heat flow data monitored by these both techniques allows determination of the kinetic parameters of the decomposition process which describe the rate of the heat generation in the conditions of the ideal heat exchange with the surroundings. However, the correct scale-up of the results obtained by DSC or HFC requires the application of the proper heat balance in the simulated system. In kg-scale, due to increasing sample mass, the conditions of the heat exchange with the environment significantly changes what, in turn, may significantly increase the reaction rate and the spatial evolution of the sample temperature [2].

Presented study illustrates the basic principles of a new kinetic analysis workflow in which the heat flow traces collected in mg-scale (e.g. DSC) are simultaneously considered with the results of investigations performed in kg-scale as e.g. UN H.1 or H.4 [1] or explosion tests (cookoff) frequently performed for civil or defence applications. Application of the newly proposed kinetic workflow may help in more precise scale-up increasing therefore the accuracy of simulations of large-scale experiments and determining more accurate temperature of explosion and thermal hazard indicators. It also considerably decreases the amount of expensive and time consuming experiments in kg-scale.

New kinetic approach is illustrated by the simulation of SADT values. The simulation results were verified experimentally by the series of large-scale experiments (UN test H.1) performed with packages of 5, 20 and 50 kg of Azobisisobutyronitrile (AIBN) in an oven at constant temperatures. Additionally, the simulations computed by the new method were verified by the results of the cook-off experiments carried out with ca. 0.3 kg of single-base propellants in cylindrical steel tubes with either heating rates of 3.3 and 1.0 K h^{-1} or under isothermal and heat-wait-search conditions. The thermal behaviour simulations were compared with the experimental data showing good fit to both, heat flow traces (mg-scale) and time to ignition (kg-scale). The influence of shape (rectangular box, drums with various *H*/*D* (*H*: height, *D*: diameter) ratios and equivalent sphere), sample mass and overall heat transfer coefficient on the SADT values and runaway time were additionally simulated (AKTS-Thermokinetics and Thermal Safety Software [3]) and discussed.

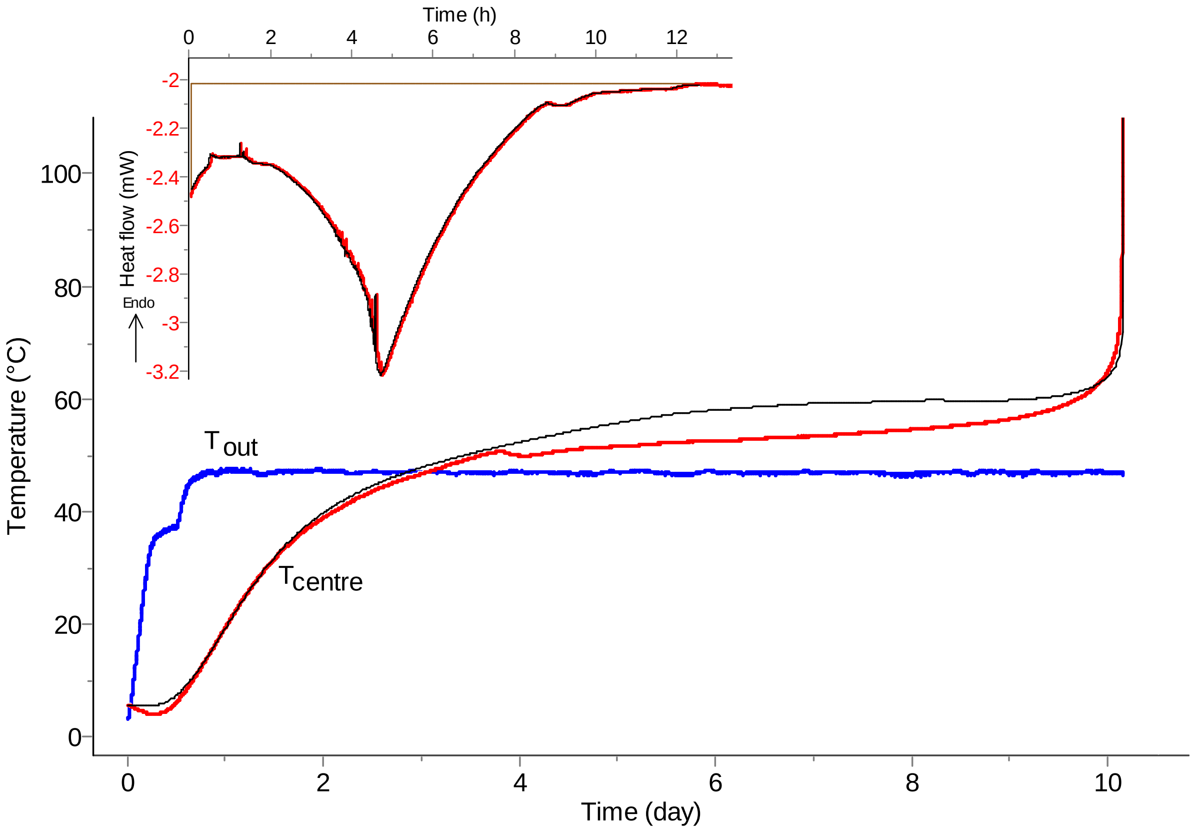

Fig. 1 Experimental (bold/red) vs. simulated (thin/black) behavior of AIBN in mg- and kg-scale: DSC traces of 14.5 mg AIBN decomposed isothermally at 80°C (Inset (exo down, German DIN standard)) and temperature in the centre of 50 kg AIBN placed in a drum (filling height *H* = 46 cm and *D* = 46 cm) heated in an oven at 47°C (bold/blue) with corresponding thermal runaway event after ca. 10 days. The simulations were done using the newly introduced kinetic approach based on simultaneous application of DSC signal and temperature-time dependence recorded in large-scale test.

[1] UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 5th revised edition, United Nations, New York and Geneva, 2009, 28.3.7.
[2] B. Roduit, M. Hartmann, P. Folly, A. Sarbach, P. Brodard, R. Baltensperger, Determination of thermal hazard from DSC measurements. Investigation of Self Accelerating Decomposition Temperature (SADT) of AIBN, J. Therm. Anal. Calorim., 117 (2014) 1017-1026.
[3] http://www.akts.com/thermokinetics.html and http://www.akts.com/thermal-safety.html